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Microencapsulation of fragrant oil via *in situ* polymerization: effects of pH and melamine-formaldehyde molar ratio

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Microcapsules containing fragrant oil (Foral oil) were synthesized via the *in situ* polymerization method using melamine-formaldehyde (M-F) as a wall material. The encapsulation efficiency and other physical properties were analysed with varying formaldehyde/melamine (F/M) mole ratio and pH of emulsion medium. The pH of the reaction medium was varied from 5.0–6.0 and the F/M molar ratio, 2.3 ~ 5.5. Microcapsules containing fragrant oil were synthesized successfully and their particle sizes ranged from 12–15 μm. Encapsulation efficiency of fragrant oil varied from 67–81%. It was found that both pH and F/M molar ratio have an effect on the separation of M-F pre-polymer, consequently the morphology of the surface of the microcapsule was changed as well as encapsulation efficiency. The encapsulation mechanism, focusing on the liquid–liquid phase separation of methylolmelamines and formation of M-F precursor particle, was described to explain the surface morphology and encapsulation efficiency.

Keywords: Microcapsule, fragrant oil, melamine-formaldehyde, *in situ* polymerization, precursor particle, morphology, encapsulation efficiency.

Introduction

Microcapsules can be defined as containers which can release, protect, and/or mask various kinds of active materials, for example coated granules and pellets. Various products have been devloped (Shioi *et al.* 1985, Seitz 1993, 1995). Most capsule wall materials are organic polymers, such as gelatin, urea-formaldehyde (U-F), polyurethane and melamine-formaldehyde (M-F), but fats and waxes are also used (Kasai and Koishi 1977, Scher 1983). In this work, the *in situ* polymerization method using M-F was used for the encapsulation of fragrant oil. With *in situ* polymerization, no reactive materials are added to the core material. Polymerization occurs exclusively in the continuous phase and on the continuous phase side of the interface formed by the dispersed core material and continuous phase. Polymerization of reagents located there produces a relatively low molecular weight pre-polymer. As this pre-polymer grows in size, it deposits on the surface of the dispersed core material being encapsulated, where polymerization with crosslinking continues to occur, thereby generating a solid capsule

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shell (Benita 1996). This kind of encapsulation method is adequate for the encapsulation of water-immiscible oils with M-F, which shows good water-resistance, thermostability and chemical-resistance. However, there are few research works on the effect of reaction conditions of M-F pre-polymer on the encapsulation of fragrant oils. Encapsulations were conducted via two steps: preparation of stable fragrant oil emulsions and *in situ* polymerization using M-F. After the preparation of microcapsules, particle size, encapsulation efficiency, morphology, and thermo-mechanical properties were measured for the investigation of the effect of M-F pre-condensate characteristics and pH of the medium on the final properties of the microcapsules.

Experimental

Materials

Floral oil was received from FKA Korea Co. and used as core material (fragrant oil). As shell materials, melamine (Lancaster, UK) and formalin (37% formaldehyde solution, Yakuri Pure Chemical, Japan) were used without purification. Arabic gum (Daejung Chemical, Korea), sodium lauryl sulphate (SLS, Duskan Chemical, Korea), and Tween 20 (Daejung Chemical, Korea) were used as stabilizers and/or surfactants. For pH control, sodium hydroxides (NaOH, Duksan Chemical, Korea) and citric acid (Duksan Chemical, Korea) 0.5 N aqueous solution were used. DDI (double-distilled and deionized) water was used throughout.

Preparation of M-F pre-polymer

A calculated amount of melamine and formaldehyde was injected in 500 ml 3-neck rounded flask equipped with mechanical stirrer and condenser. The reaction mixture was heated to 85°C and the pH of the mixture was adjusted at 8.7 ~ 8.9 using 0.5 N NaOH solution. Appropriate reaction time was determined by gravimetric determination of unreacted residual formaldehyde. The basic recipe for the preparation of M-F pre-polymer and fragrant oil emulsion is given in table 1.

Preparation of fragrant oil emulsion

Pre-determined amounts of Arabic gum, SLS, and Tween 20 were dissolved in DDI water, and fragrant oil was added. The emulsion of the fragrant oil was prepared using an homogenizer (Omni Macro Homogenizer, Omni Int., USA) with 2000 ~ 5000 rpm at room temperature.

Microencapsulation

Encapsulation of the fragrant oil was carried out in a 1L-rounded flask via *in situ* polymerization. The initial pH of the emulsion mixture was adjusted to ~ 7.5 using 0.5 N NaOH solution followed by addition of M-F pre-polymer. For the polycondensation of the separated M-F pre-polymer from the aqueous phase, the pH of the emulsion was gradually decreased under different acid conditions (pH = 5.0, 5.5 and 6.0) using 0.5 N citric acid solution for 2 h at 50°C. After the completion of the encapsulation reaction, 5 ~ 6 drops of methanol was added as a

Table 1. Basic r

Ingredients	
Melamine-formaldehy	
DDI Water	
Melamine	
Formalin (formaldeh	
NaOH (0.5 N aqueo	
Emulsification	
DDI water	
Fragrant oil	
Arabic gum	
SLS	
Tween 20	
Microencapsulation	
M-F pre-polymer	
Emulsion	
NaOH (0.5 N aqueo	
Citric acid (0.5 N aq	

[a,b] Formaldehyd
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[c] Appopriate am
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Emulsion-F

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Figure 1.

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Characterization

The conversio
M-F pre-polymer

Table 1. Basic recipe for the preparation of M-F pre-polymer and microcapsules.

Ingredients	Amount (g)
Melamine-formaldehyde pre-polymer	
DDI Water	41.6
Melamine	Variable [a]
Formalin (formaldehyde 37% solution)	Variable [b]
NaOH (0.5 N aqueous solution)	Variable [c]
Emulsification	
DDI water	100.0
Fragrant oil	40.0
Arabic gum	2.0
SLS	1.0
Tween 20	1.0
Microencapsulation	
M-F pre-polymer	25
Emulsion	100
NaOH (0.5 N aqueous solution)	Variable [c]
Citric acid (0.5 N aqueous solution)	Vriable *c*

[a,b] Formaldehyde/melamine (F/M) molar ratio was 2.3, 3.7, 5.5. Total weight of two ingredients was fixed at 100.0 g.

[c] Appopriate amounts of these ingredients were used to adjust the pH of the reaction medium.

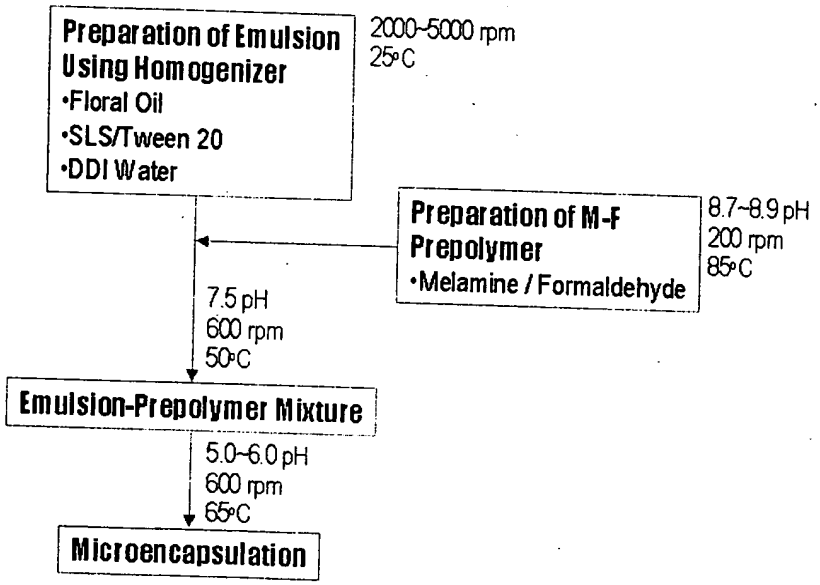


Figure 1. Schematic representation of microencapsulation process.

quencher. A small amount of Arabic gum was added to prevent the destabilization of the microcapsules. The overall preparation scheme is illustrated in figure 1.

Characterization

The conversion or residual concentration of formaldehyde in the synthesis of M-F pre-polymer was determined using gravimetry. The separation point of the

M-F pre-polymer with varying pH of the continuous medium was measured by a turbidity meter (TPS, WP89, Envioequip, Australia). Particle size and morphology of the microcapsules were measured using optical microscopy (E 600 POL, Nikon eclipse, Japan) and scanning electron microscopy (SEM, JSM-5400, JEOL Co., Japan). Encapsulation efficiency was measured by thermogravimetric analysis (TGA-50, Shimadzu, Japan). In this work, fragrant oil evaporated from the dried capsules above 120°C was defined as encapsulated oil. The encapsulation efficiency was defined as follows:

$$\textit{Encapsulation efficiency}\ (\%) = \frac{\textit{Encapsulated oil}\ (g)}{\textit{Total oil used}\ (g)} \times 100(\%)$$

The hardness of M-F polycondensate was measured by the Vickers hardness method. Oil loss of dried microcapsules was characterized by gravimetry after drying at 150°C for 5 min. Thermostability of the capsules was characterized using differential scanning calorimeter (DSC) under nitrogen atmosphere. Weights were ~ 10 mg, heating rate, 5°C/min, and the temperature range from 0–300°C.

Results and discussion

Melamine formaldehyde pre-polymer

The representative overall reaction scheme of M-F pre-polymer is illustrated in figure 2. The M-F pre-polymer is well known as methylolmelamine. Two main steps are involved in the preparation of the M-F precursor (Jahromi 1999). First, nucleophilic addition reactions of melamine to formaldehyde under basic conditions result in random substitution of the amino groups and then to the synthesis

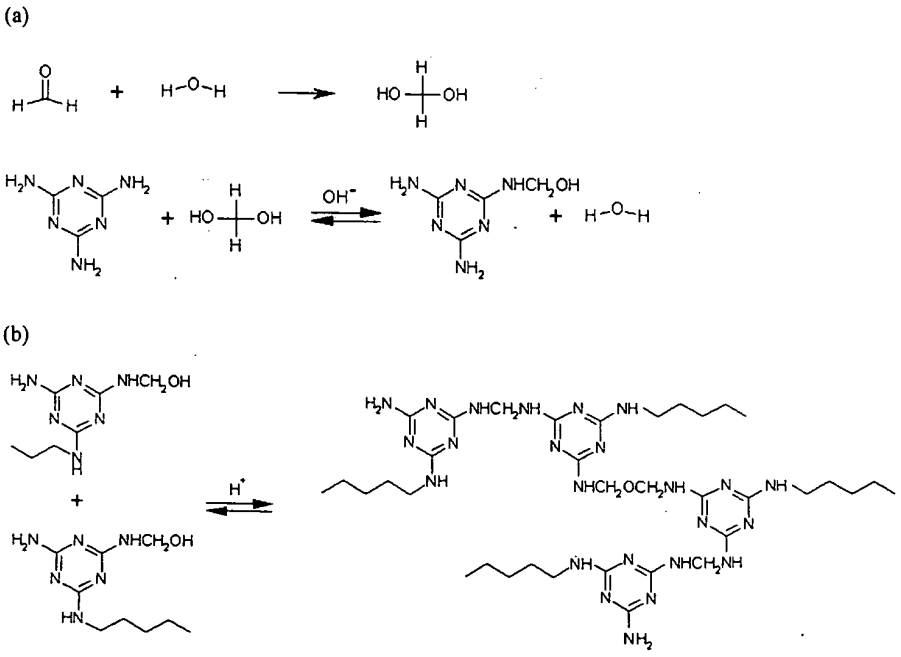


Figure 2. Overall reaction scheme of melamine-formaldehyde.

of a mixture of methylolmelamine water-solubles. Next, two different types of linkage can result from the oligomerization by the formation of bridges between triazine rings: either between two methylol groups producing a methylene ether bridge or between a methylol group and an amino group producing a methylene bridge. Then, a large number of oligomeric derivatives and crosslinked network during polycondensation reaction are formed (Kumar and Katiyar 1990, Coullerez *et al.* 2000). These bridge formations can be affected by many reaction parameters, such as pHs, F/M molar ratio, reaction temperature, and solid content. It is difficult to represent a M-F unit with a clear chemical structure and a well-defined repetition unit because of the wide variation in functionality, structure and reactivity of the intermediates involved in the reaction.

Figure 3 shows the residual formaldehyde (wt% based on initial formaldehyde) against the reaction time. The F/M molar ratio was varied from 2.3–5.5. During the reaction, formaldehyde monomer was consumed almost linearly. As the F/M molar ratio increased, content of the residual formaldehyde increased and the reaction reached an equilibrium state earlier. Arrows in figure 3 indicate the beginning of the reaction equilibrium state. Even at 1.1 F/M molar ratio, a small amount of formaldehyde monomer still remained without participating in the methylolmelamine formation reaction. It was expected that this residual formaldehyde would react with water-soluble methylolmelamine to form water-insoluble precursor particles.

Separation of M-F pre-polymer

M-F pre-polymer, in other words methylolmelamine mixture, is water-soluble initially the pH of the reaction mixture was adjusted to 5.0 and 8.0 at the beginning of the reaction for the investigation of pH effect. Turbidiy of the pre-polymer

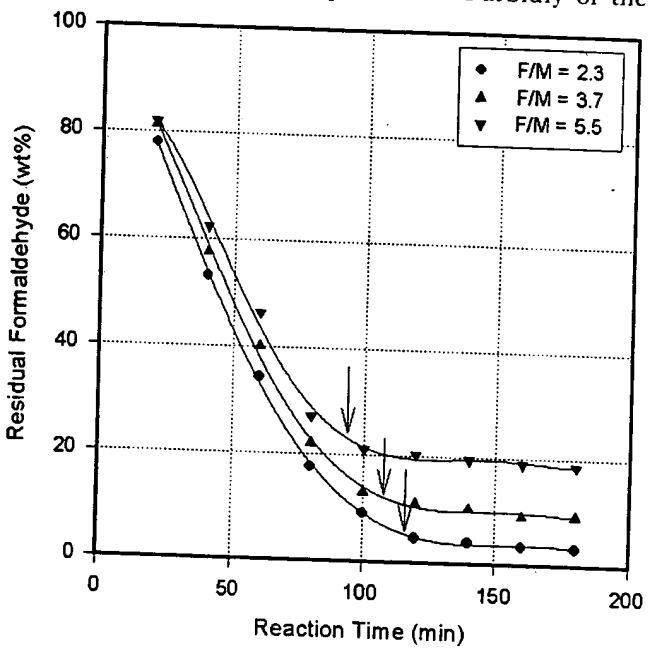


Figure 3. Residual formaldehyde against different F/M molar ratio in the preparation of M-F pre-polymer.

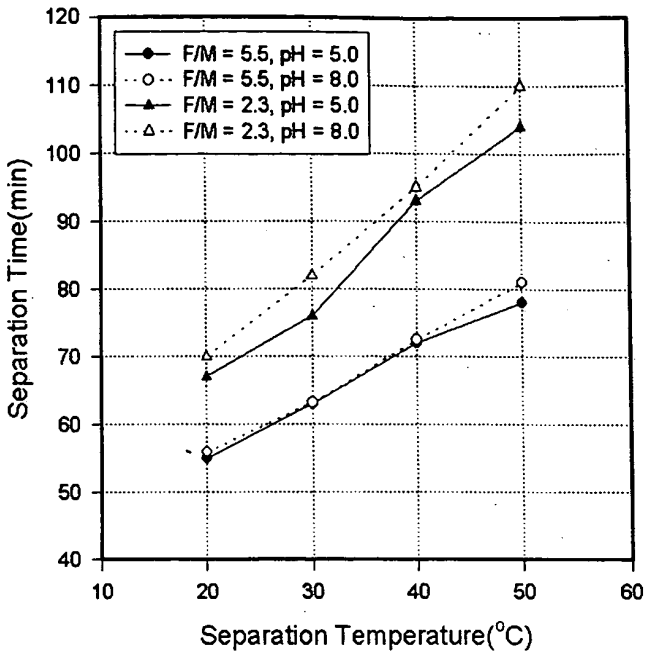
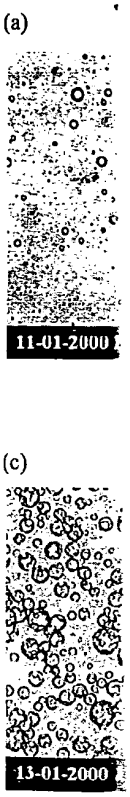


Figure 4. Separation temperature and time for M-F precursor with varying F/M molar ratio and pH.

solution was monitored continuously without further pH adjustment with varying temperature. As the bridging reaction proceeds, solubility of the pre-polymer mixture decreased and eventually separated from its original continuous medium. Figure 4 shows the effects of F/M molar ratio and pH of the continuous medium on the separation condition. Solubility of the pre-polymer mixture increased as the reaction temperature increased. As can be seen in figure 4, at a high F/M molar ratio, the separation time was shortened at a constant reaction (for separation) temperature. In principle, two different types of bridges may be formed leading to methylene or ether bridges according to the pH and F/M molar ratio, which affects the solubility of the pre-polymer mixture (Kumar and Katiyar 1990). Ether bridges can be formed easily in a high F/M mole ratio, as illustrated in figure 2, and it was expected that methylolmelamine derivatives with high functionalities would be obtained easily at a high F/M molar ratio. It can be seen that the F/M molar ratio depends on the separation temperature at the same reaction time, whereas the pH effect is not so significant. At low pH, the pre-polymer mixture became turbid rapidly. However, it was observed that neither separation temperature nor time depends on pH of the reaction medium. As mentioned above, pH was not adjusted but it decreased continuously during the reaction. The pH decreased during the reaction, which was attributed to the formation of formic acid according to the so-called Canizarro reaction (Jahromi 1999). Eventually, this reaction reduced the pH to accelerate the polycondensation of M-F pre-polymer.

Characteristics of microcapsules

Figure 5 shows Floral oil emulsion (*a*) and microcapsules (*b*), (*c*) and (*d*), with varying pH at a 5.5 F/M molar ratio. The droplet size of the floral emulsion ranged



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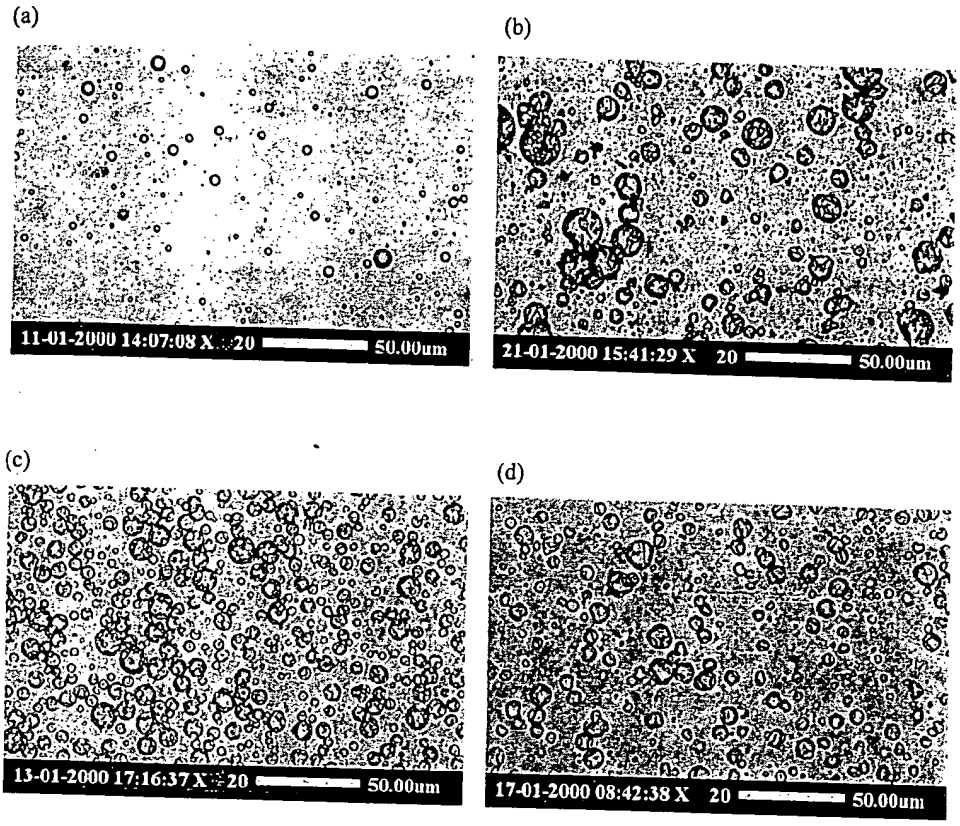

Figure 5. Optical microscopy photographs of fragrant oil droplet (*a*) and microcapsules prepared with different pH; (*b*) 5.0, (*c*) 5.5, (*d*) 6.0.

from 3–8 μm. The average particle size depends on surfactant (or stabilizer) level/type, homogenizer speed/time, and type of oil. After the preparation of the stable emulsion, M-F pre-polymer was injected at 50°C. The pH in the encapsulation process varied from 7.5 to 5.0 (*b*), 5.5 (*c*) 6.0 (*d*), respectively, in figure 5 using 0.5 N citric acid solution. The average particle size of the microcapsules was 15 (*b*), 13 (*c*), and 12 μm (*d*), respectively. As pH increased, the average particle size of the microcapsule decreased and its surface became smooth. At low pH, the surface morphology of the microcapsule decreased and its surface became smooth. At low pH, the surface morphology of the microcapsules was similar to that of a raspberry. This suggested that aggregates or premature particles, which were formed from condensation reaction among methylolmelamine oligomers, adsorbed onto the oil droplets. Further condensation reactions between the premature particles on the droplet surface consolidates the wall of the capsules. As mentioned earlier, the formation of methylene bridge is favourable at low pH, whose water-solubility would be lower than that of ether bridges. Therefore, individual particles consist of network M-F precursors that can be formed immediately without liquid–liquid separation from the aqueous phase onto the oil droplet interface.

Capsulation efficiency

The existence of floral oil in the microcapsule was easily verified by optical microscopy. Figure 6 shows microcapsules containing floral oil (*a*) and released floral oil and cracked microcapsules (*b*) under pressure. Table 2 shows the capsulation efficiencies of the floral oil with varying pH and F/M molar ratio. It was found that the pH did not significantly affect the efficiency. However, as the F/M molar ratio increased from 2.3 to 5.5, the efficiency increased. The efficiency was not determined solely by the separation condition of methylomelamine but by both F/M molar ratio and pH. A high encapsulation efficiency can be obtained when the wall material shows good thermo-mechanical resistance. In fact, microcapsules prepared under low F/M molar ratio and low pH were crushed easily during the drying process by gravity. It was found that the low value of the efficiency was mainly attributed to deformation of the shell during the heating and drying process. Oil loss was measured by gravimetry under the conditions of 5 min and 150°C. The oil loss increased from 6–25wt% when the F/M molar ratio decreased from 5.5 to 2.3. As can be seen in table 3, it can be expected that high F/M molar ratio gives low hardness but high flexibility. As the F/M molar ratio decreased, however, the M-F polycondensate became more brittle.

Figure 7 shows the DSC curves for the microcapsules prepared with varying F/M molar ratio. As can be seen in figure 7, the main relaxation peaks were shifted

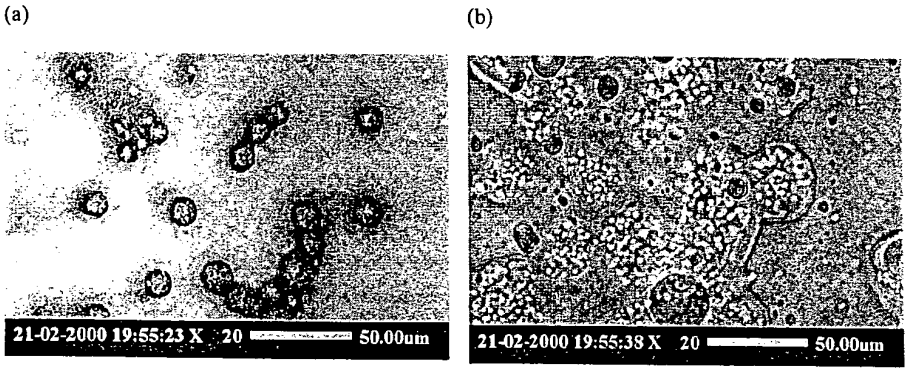

Figure 6. Optical microscopy photographs of dried microcapsules (*a*) and released fragrant oil and crushed capsules under pressure (*b*).

Table 2. Encapsulation efficiency with varying F/M molar ratio and pH.

Process variables	Encapsulation efficiency (%)
At 6.0 pH	
F/M = 2.3	67.2
F/M = 3.7	72.1
F/M = 5.5	81.4
At F/M = 5.5	
pH = 5.0	73.8
pH = 5.5	76.0
pH = 6.0	81.4

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Table 3. Hardness with varying F/M molar ratio.

F/M molar ratio	Hardness[a]
2.3	23
3.7	14
5.5	10

[a] Hardness of copper: 30 ~ 40; steel: 100.

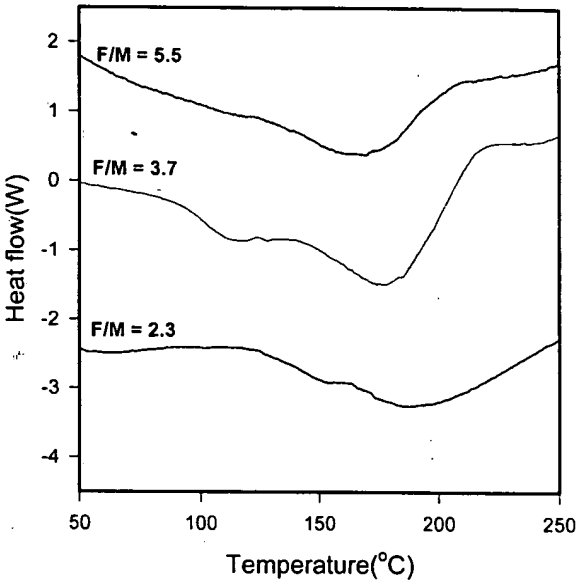

Figure 7. DSC curves of microcapsules containing floral oil with varying F/M molar ratio.

to a higher temperature region as the F/M molar ratio decreased. All these transition temperatures were higher than 150°C.

Figure 8 shows the microcapsules containing Floral oil which were prepared under different pH and F/M molar ratios. The pH values in figure 8(*a*) and (*b*) are 6.0 and 5.0, F/M molar ratio 5.5 and 2.3, respectively. It was observed that surface morphology of the microcapsules was different with varying F/M molar ratio and pH of the reaction medium. As the pH decreases, formation rate of M-F precursor increases consequently to accelerate the formation of individual M-F particles during the phase separation (Samejima *et al.* 1982). A number of small M-F particles were observed in the case of low pH and F/M molar ratio. The surface of microcapsules in figure 8(*b*) was raspberry-like and seemed to be composed of aggregates of the M-F particles. This polynuclear morphology has been reported by Sheiham and Templey (1992) in the preparation of microcapsules for carbonless paper. From this result, it was expected that a competitive reaction occurred between the separation/solidification of M-F precursor and the formation of individual M-F particles in the aqueous phase. It was concluded that the separation condition of M-F pre-polymer significantly determined the surface morphology and encapsulation efficiency.

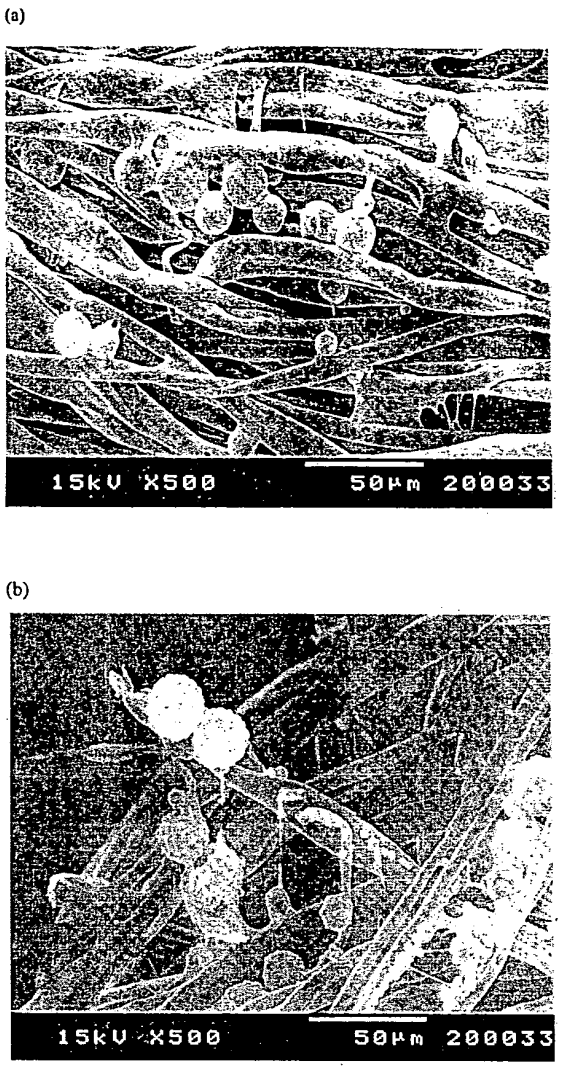

Figure 8. SEM image of microcapsules containing floral oil attached onto the cotton fibre; (*a*) pH = 6.0, F/M = 5.5; and (*b*) pH = 5.0, F/M = 2.3.

Acknowledgements

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